Nano-Thermoelectric Devices Fabricated by Ion Beam Writing

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14. ABSTRACT
A lithographic process has been developed to construct the suspended structure. The self-heating 3W method and measurement systems for nanoscale material have been constructed. The thermal conductivity and specific heat of diameter of 180nm nickel sire are 23 W/m-K and 64.6 J/mol-K (at 25C), respectively. A 30 nano-wire has been fabricated for concept demonstration.

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Nano-Technology, PowerMEMS, Thermoelectric

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Nanotechnology and Energy

Improved efficiency of energy usage:

- Non-thermal energy usage, via nanostructured devices such as fuel cells;
- Molecularly tailored catalysts, for heightened selectivity and byproduct elimination;
- High-strength materials, which will decrease transportation costs;
- Electricity storage and electrosynthesis, both for portable power sources, and for chemical fuel generation;
- Distributed fabrication, to minimize transportation infrastructure.

Information-intensive energy extraction:

- Extensive real-time sensing, for better conventional resource extraction;
- Cheap nanofabrication, which will make practical distributed collection from diffuse sources, as well as better energy management through such devices as "smart windows" and non-thermal light sources

Nanotechnology and Energy

Solid-state energy generation:

- Solar power, via photovoltaics and artificial photosynthesis;
- Thermoelectric conversion, the direct solid-state transformation of thermal gradients into electricity;
- Piezoelectric conversion, for direct conversion of mechanical energy into electricity.
- Solid electrolytes—critical in fuel cells and supercapacitors; relevant to intercalation batteries, smart windows, electrocatalysis, and also to ionic separation.

***Nanoscale structuring at an interface is fundamental* to many applications, including:**

- Catalyst surfaces;
- Large-area semiconductor p-n junctions, critical to thermoelectric and photovoltaic materials;
- Nanolayered structures, such as for high-performance capacitors, thermoelectric materials, multijunction photovoltaics, piezoelectric stacks, and sensitized photosynthetic materials.

Nanotechnology and Energy System

Energy Source/Materials

- Solar Energy
- Bio-energy/ Bio-mass/Water
- Fuel/Electricity
- Thermal Structure Materials

Critical Nanotechnology

Full spectrum nanomaterials
Printable /Flexible material & substrate
Nano-scale crystalline silicon

Bio-catalyst / Biodegradable
Chirality centered material
Functional Nano-fibers

High active Bio-fuel
Nano Structual Materails for catalyst
Nanostructural Organic/Inorganic Materials
Hyper-branch catalyst Organic/Inorganic electrolyte

Nanostructure Low Phonon scattering, high ZT Materials
Surface Plasmon
Quantum well design

System Platform

Solar Cell → W~GW Systems

Hydrogen Production Storage → Car Applications

Biodegradable/Recyclable/
Renewable Materials
Clean Water Purification

Fuel-cell → W~kW Systems

Power Storage

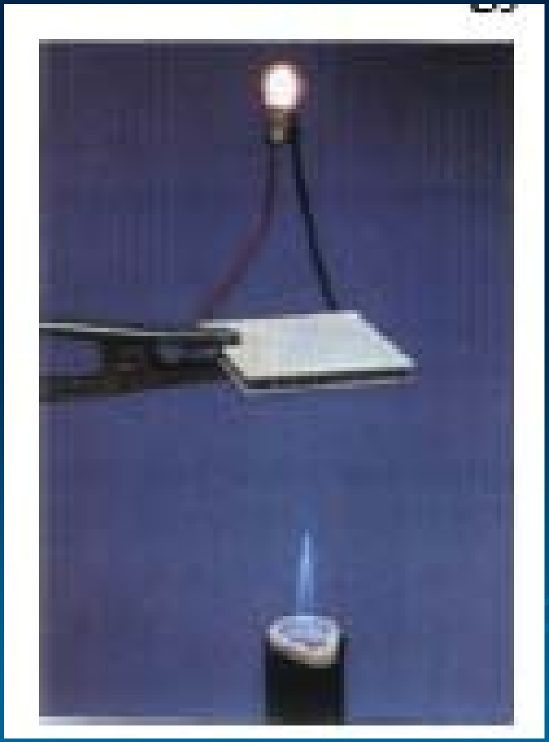
Electricity, Cooling

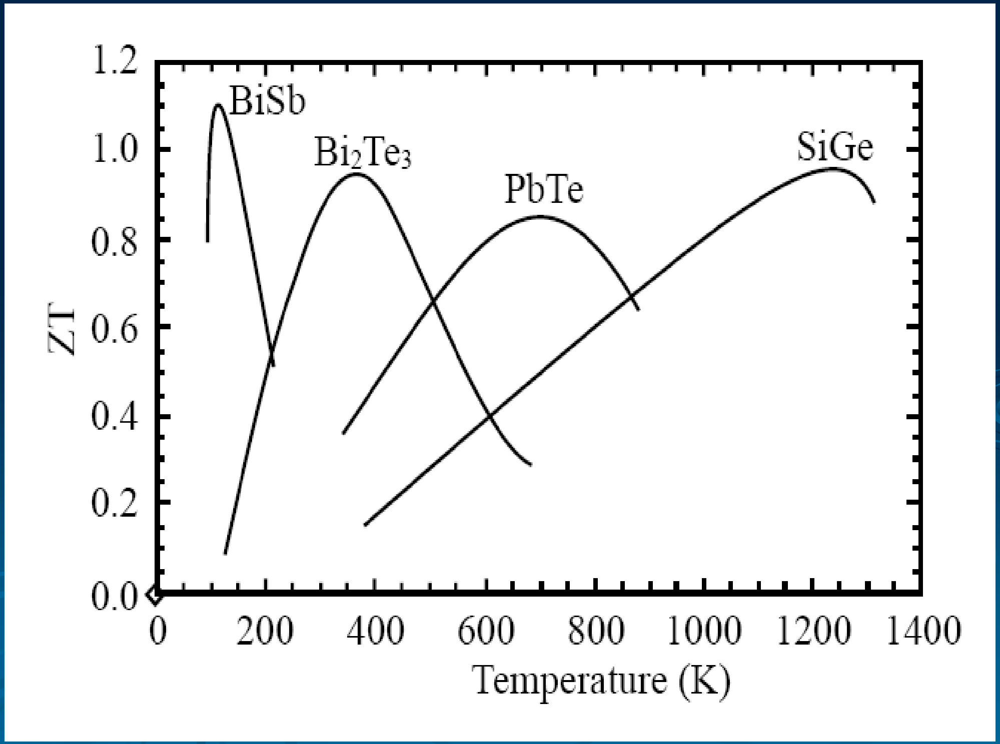
Environmental, Energy Saving

* **Energy conversion efficiency** **Figure of Merit：ZT**

$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

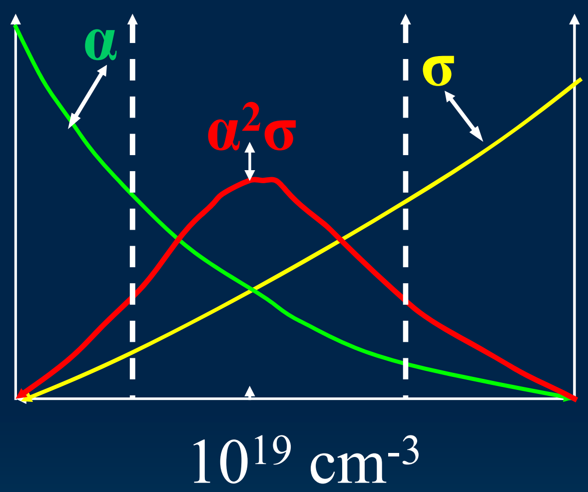
α is Seebeck Coefficient.
σ is Electric Conductivity.
κ is Thermal Conductivity
T absolute temperature

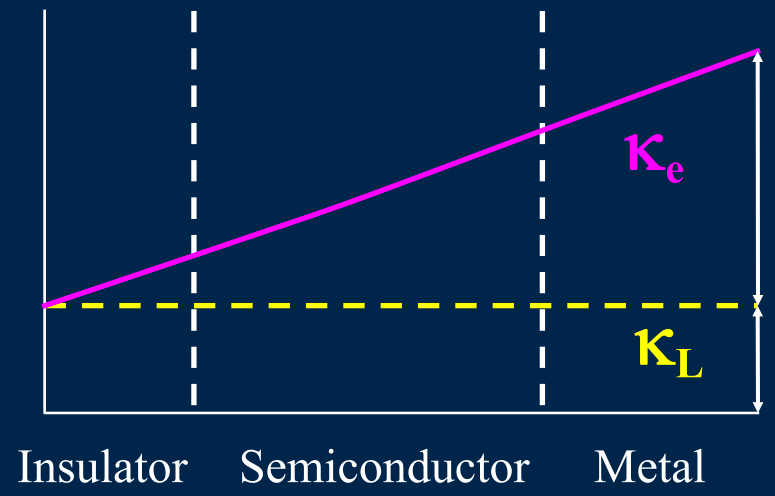




$$ZT = \frac{\alpha^2 \sigma T}{(\kappa_E + \kappa_L)}$$

* How to increase ZT ?





α,σ (D(ε), ε_F, μ)

$$\sigma / \kappa_e = 1/(L_0 T)$$

Wiedmann-Franz Law:

L_0□Lorentz num.

Reduce phonon thermal conductivity

Strategy

1. Increase Seebeck Coefficient α□ quantum size effects,

   Example: Quantum Wires in Nanostructures

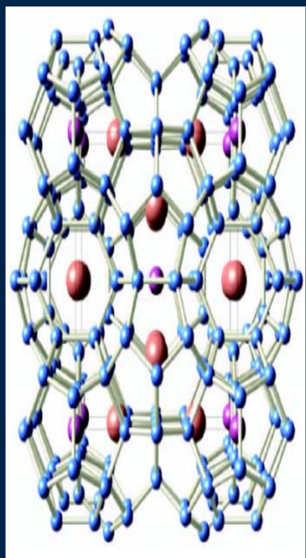
2. Reduce thermal conductivity κ_L □decrease lattice phonons mean free path.

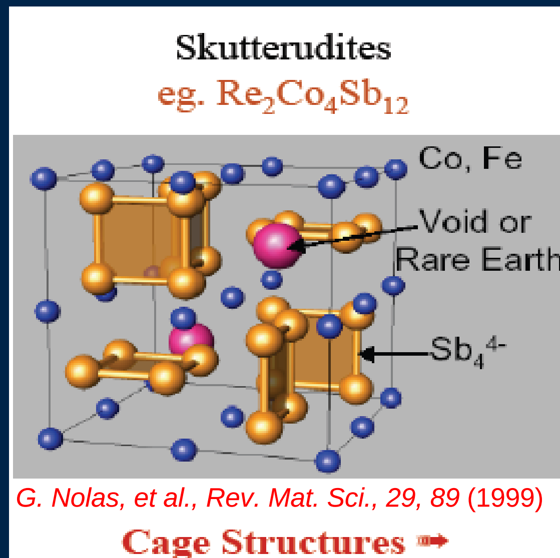
   Example: Multilayers or Superlattice , Nanostructured bulk materials (nanoparticle-dispersed composites)

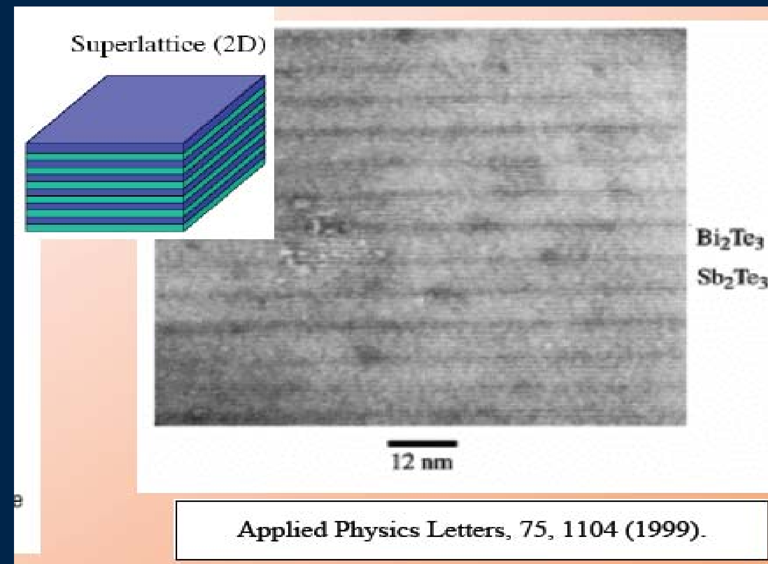
3. Directional dependent of thermal conductivity

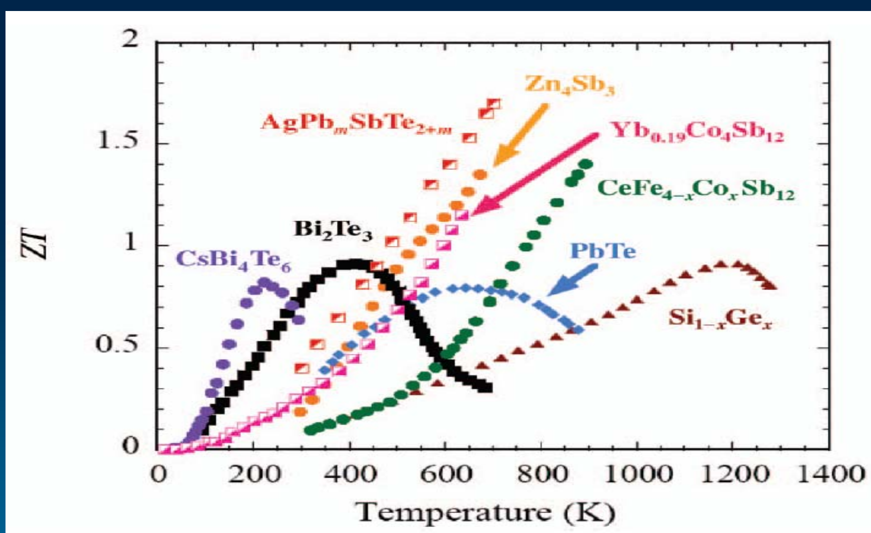
(A) Crystal Structures with "Rattlers"

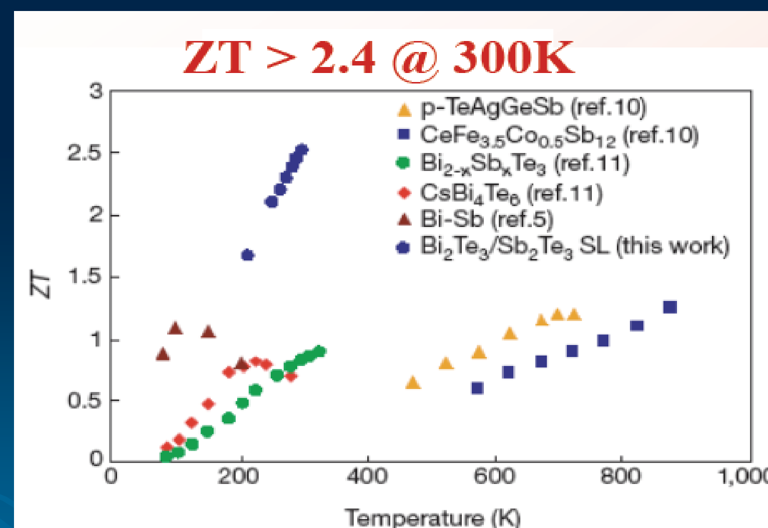
(B) Superlattice Lattices







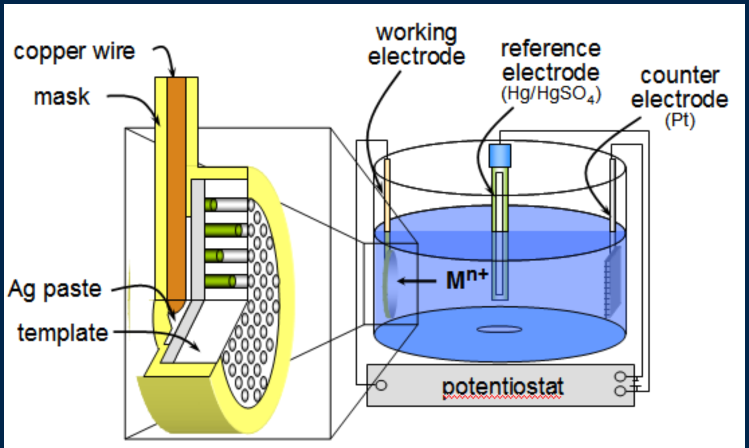




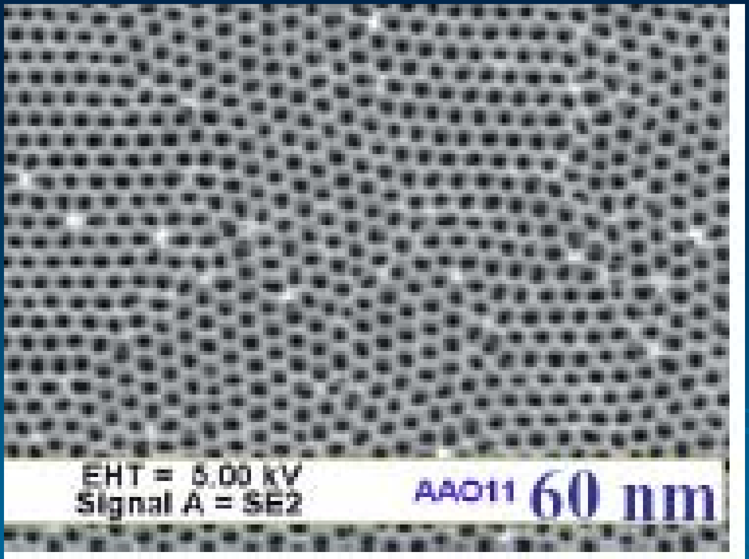
Need higher ZT ~1.5-2

Too thin and too expensive

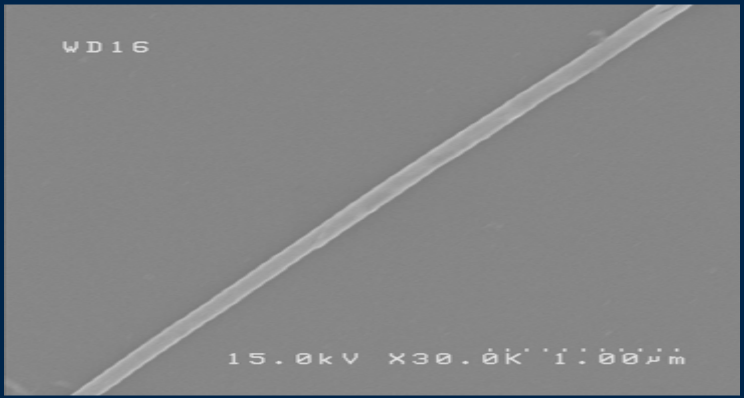
Enhancement of ZT in Nanowire Array

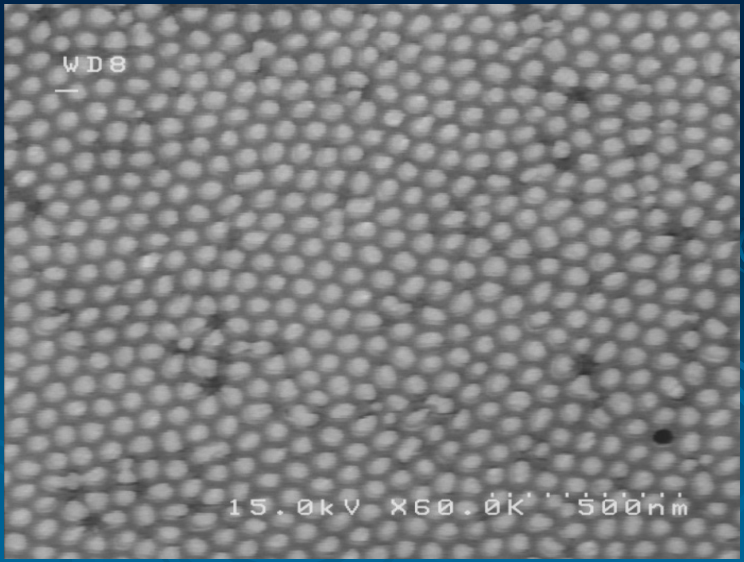


Anodic Aluminum Oxide (AAO)

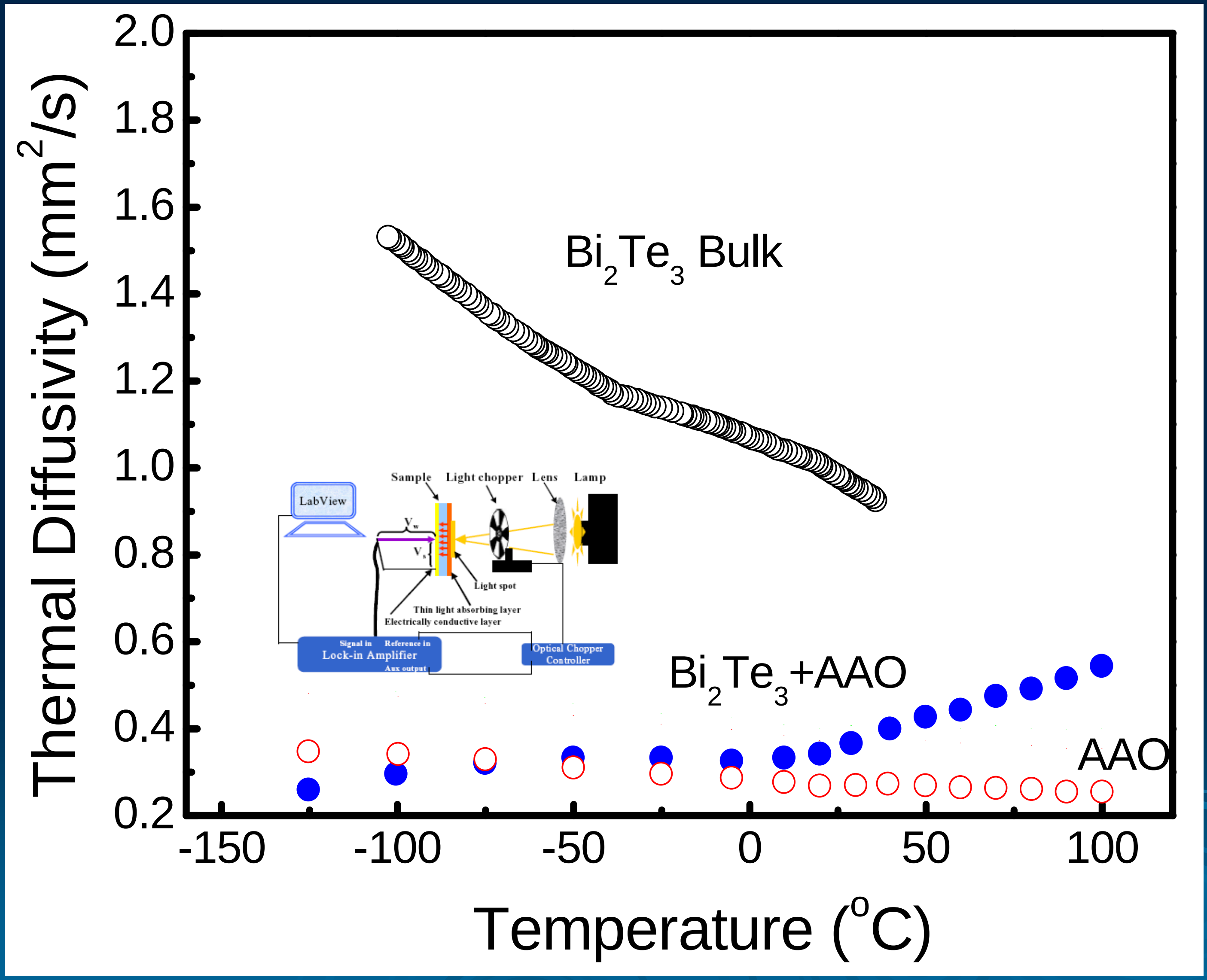


~50 nm Bi_2Te_3
Nanowire array

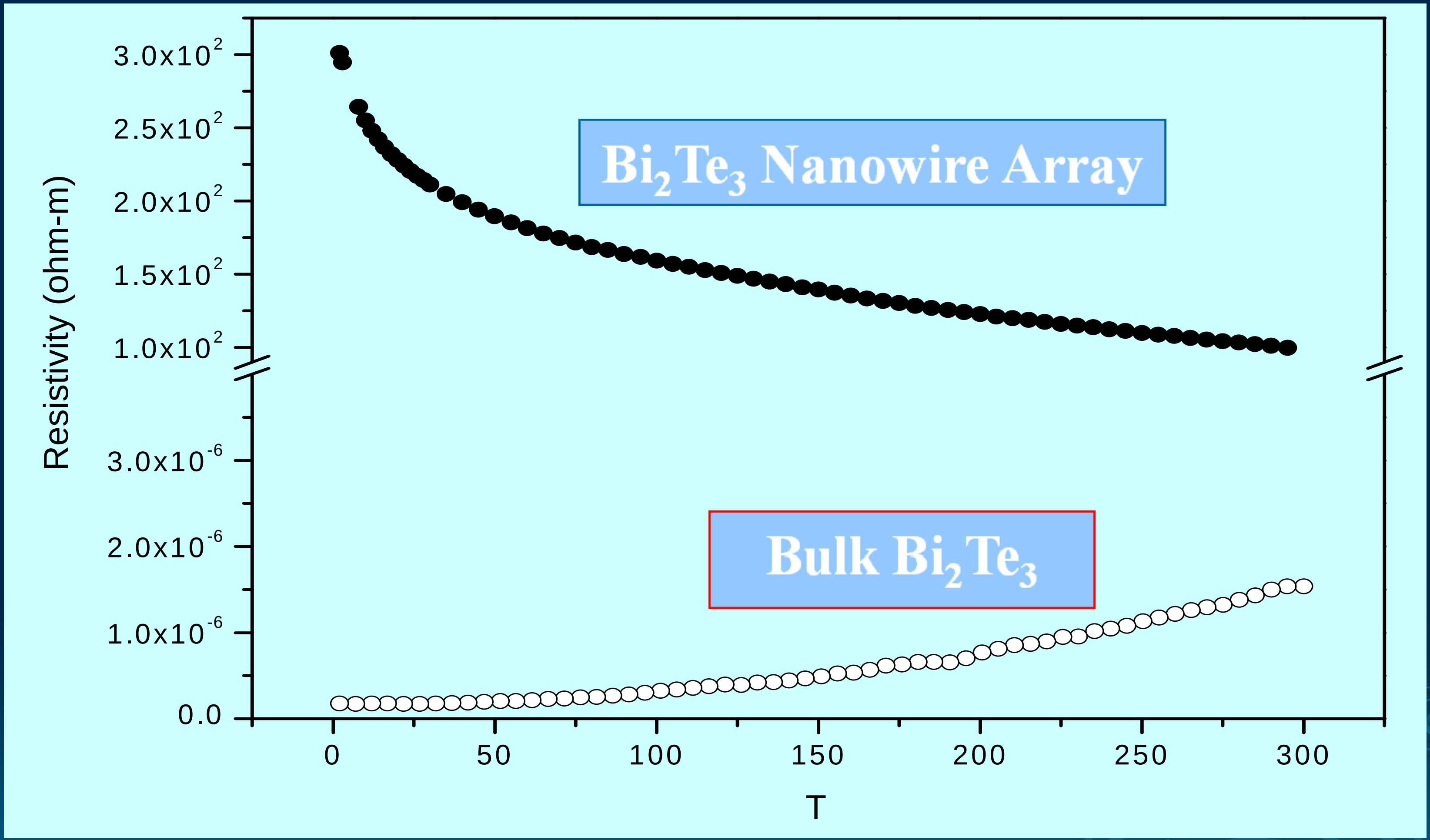




Thermal Diffusivity of Bi_2Te_3 Bulk and Nanoarray



Resistivity of Bi_2Te_3 Bulk and Nanowire Array



Need to overcome the large resistivity !!
Better quality sample ?

Action Plan

- Nanometer Bi_2Te_3 nanowires fabricated by ion-milling creating "neck" diameters close to the mean free path will be examined using the 3ω process to determine the effect of nanowire diameter on thermal conductivity properties.
- Quantifying the change in heat conduction experimentally in variable diameters provides insight to the theorized mechanisms of thermoelectric performance enhancement and advances designing practical nanothermoelectric devices.
- Experimentally study phonon heat conduction in Ion Milled Bi_2Te_3 Nanowires and 2 dimensional tapered structures to investigate significant performance advance attributed to decreasing heat conduction by phonons – without significant alterations of resistance properties.

Experimental Details—Nanowires

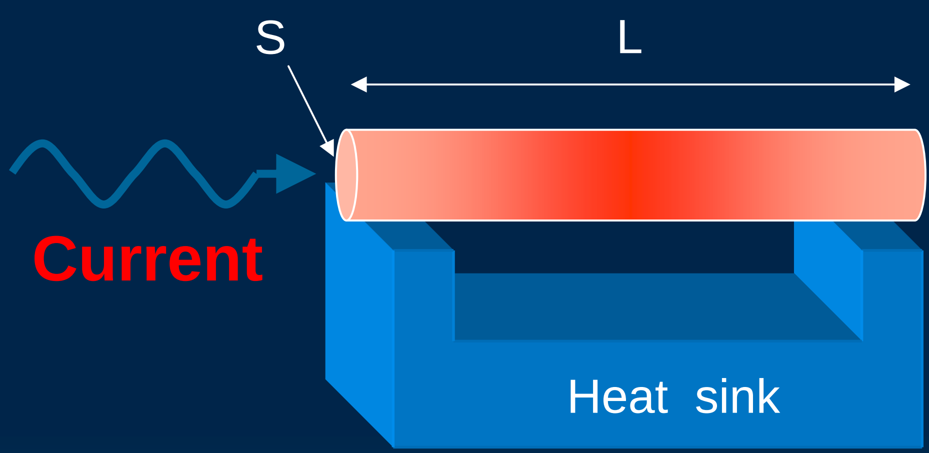
- Fabrication of one individual & suspending nickel nanowire
  - Evaporation deposition
  - E-beam lithography
  - Anisotropic Wet-Etching
- Observation for nano-scale materials
  - 3ω method
    - Electrical conductivity
    - Thermal conductivity
    - Specific heat

Self heating 3ω Method

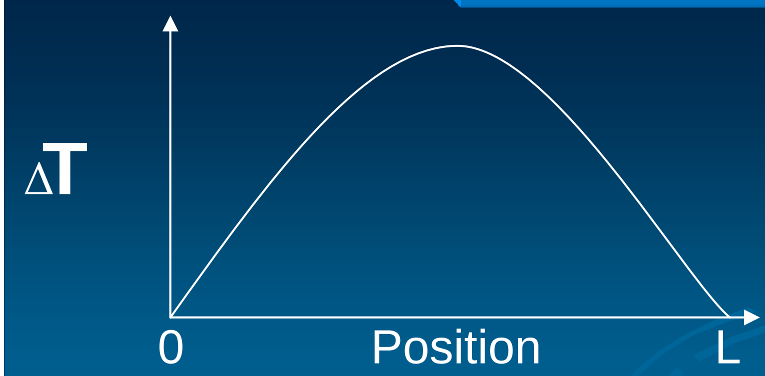
- The basic idea of the 3ω self-heating method is that when one passes an ***alternating current*** with frequency ω, it will heat the wire uniformly.
- If we make a suspension structure, as shown in the next slide, i.e., a uniform wire lies on a high thermal conductive substrate so that the ends part are contacted with substrate but middle part is not.
- It then created a temperature distribution, which with highest temperature rising at mid point and lowest at end point.
- The responded 1^{st} harmonic signal gives the information of electrical conductivity, and 3^{rd} harmonic term the temperature variation.
- Thus, parameter κ and specific heat C_p can be determined by fitting the signal of 3ω voltage with the formula.

Idea of self heating 3ω Method

$$\rho C_p \frac{\partial}{\partial t} T(x,t) - \kappa \frac{\partial^2}{\partial x^2} T(x,t) = \frac{I_0^2 \sin^2 \omega t}{LS} (R + R'(T(x,t)) - T_0)$$



ρ	density
C_p	specific heat
κ	thermal conductivity
L,S	dimension of specimen
R	Resistance
γ	time constant



$$V_{3\omega}(t) \approx -\frac{2 I_0^3 L R R'}{\pi^4 \kappa S \sqrt{1+(2\omega\gamma)^2}} \sin(3\omega t - \phi),$$

$$C_p = \pi^2 \gamma \kappa / \rho L^2$$

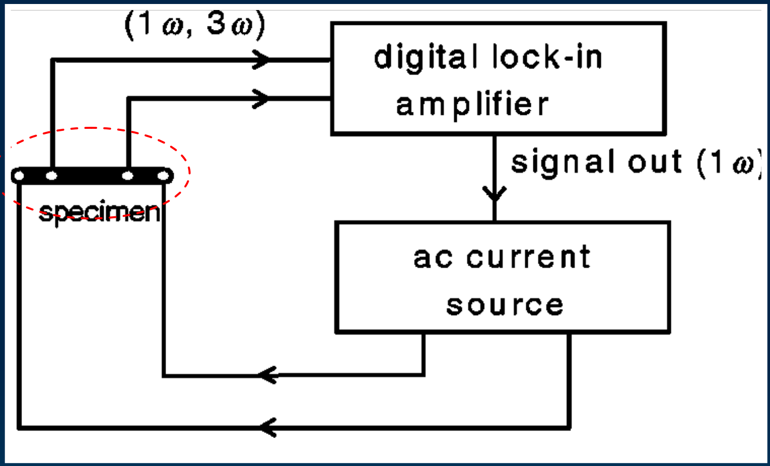
Rev. Sci. Instrum. 76, 124902 2005

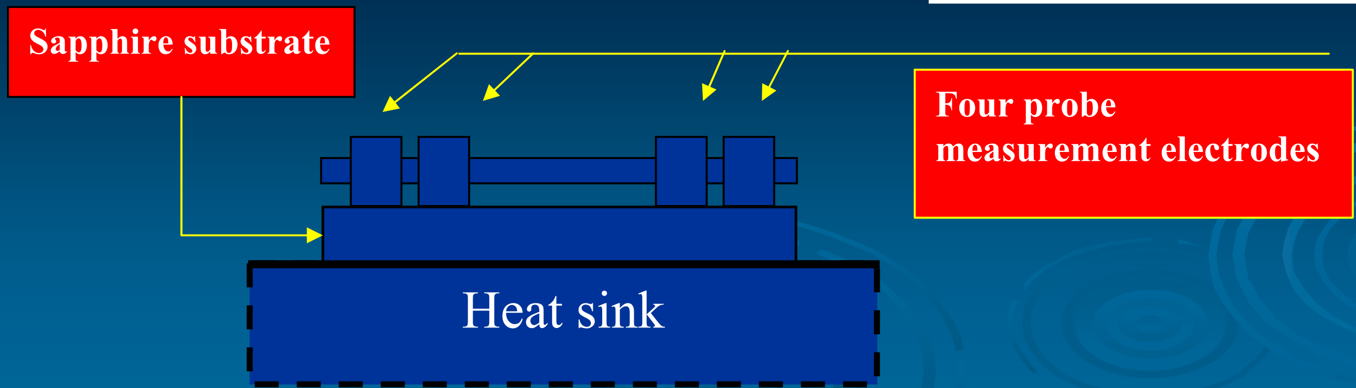
Rev. Sci. Inst. 72, 2996 (2001)

3ω Method

- To construct a measurement system of thermodynamic parameters for nanoscale specimen.

1. Suspended
2. Highly thermal conductive to heat sink
3. minimize the heat loss

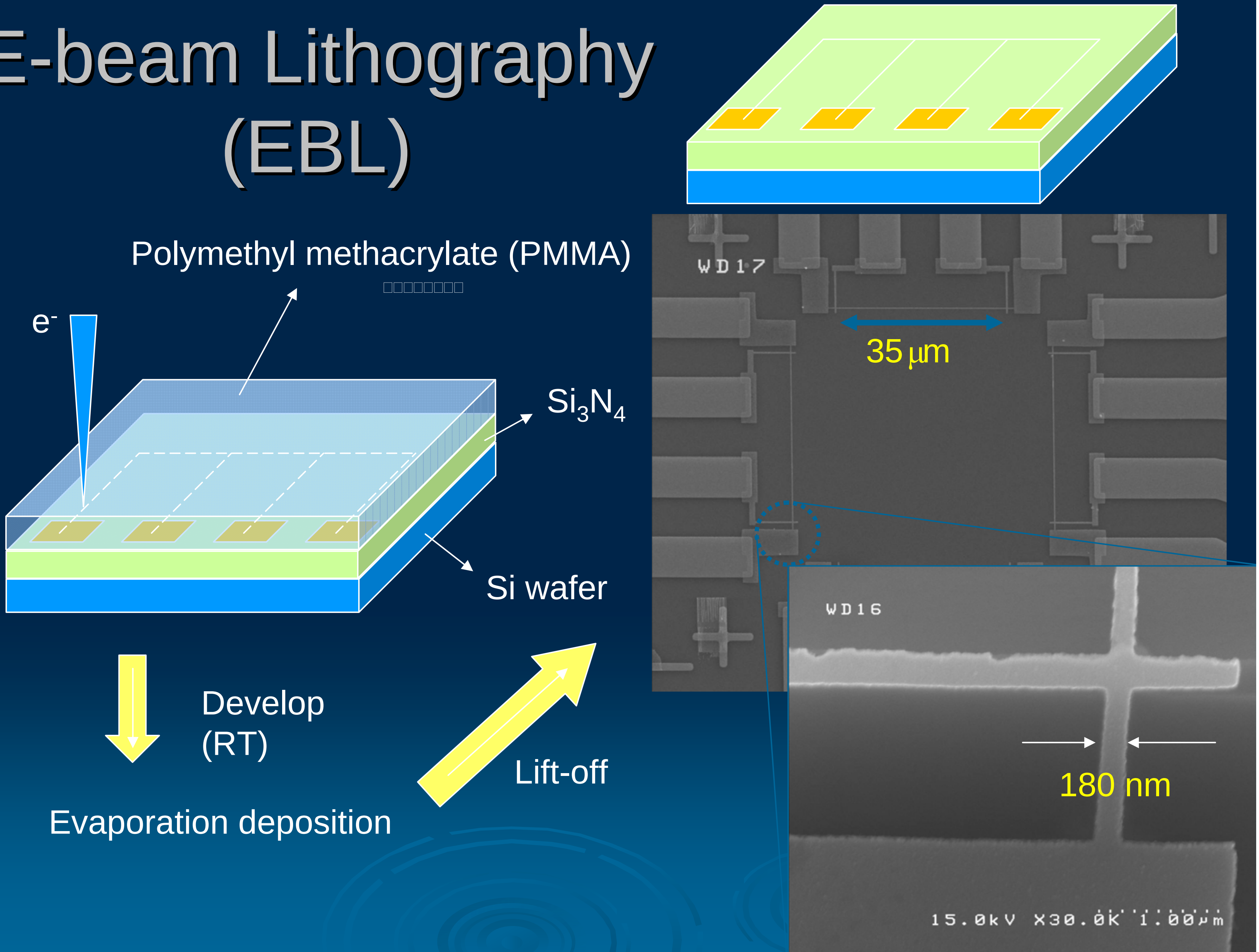




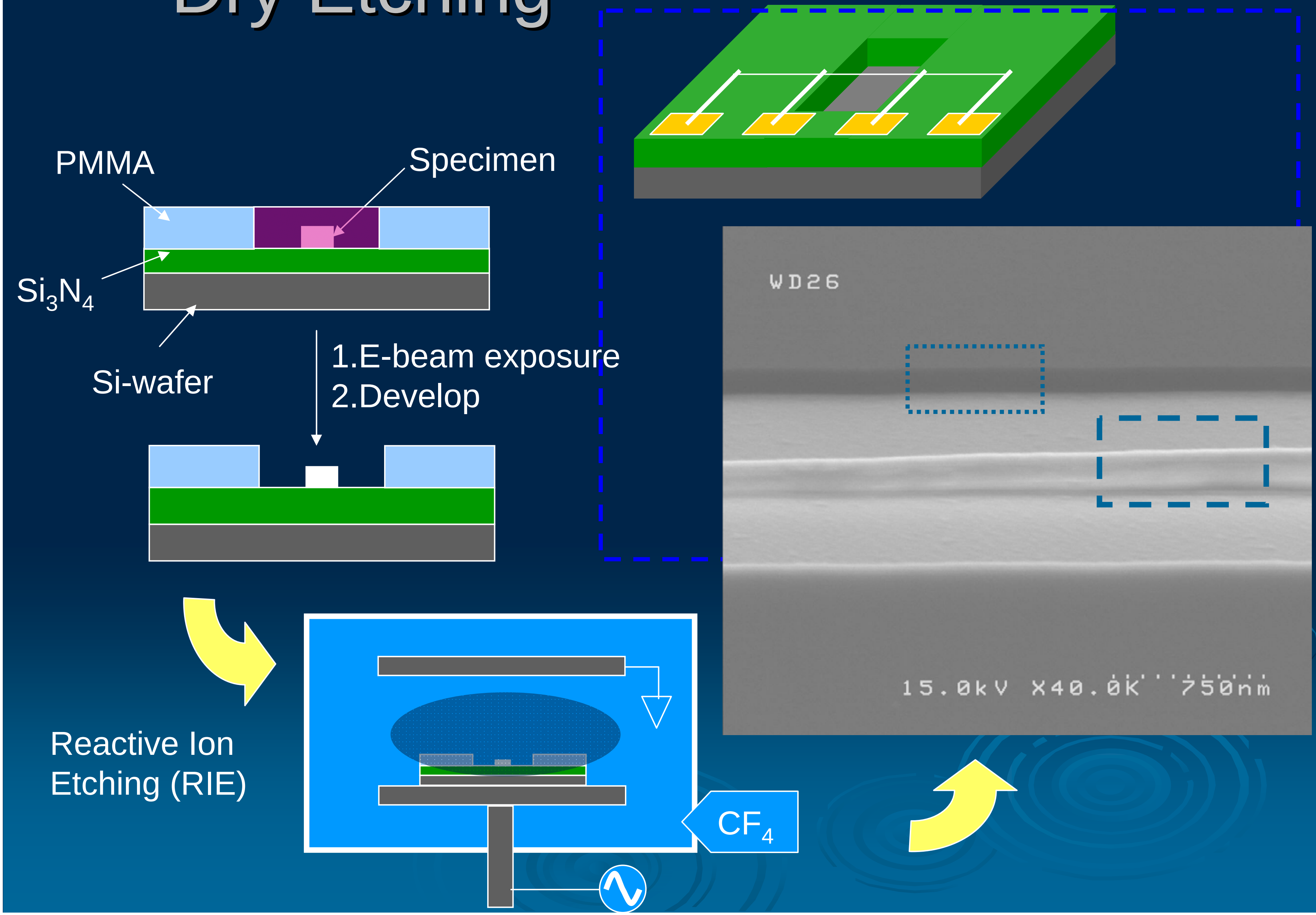
Fabrication of Individual Nanowire—Nickel

E-beam lithography & evaporate deposition

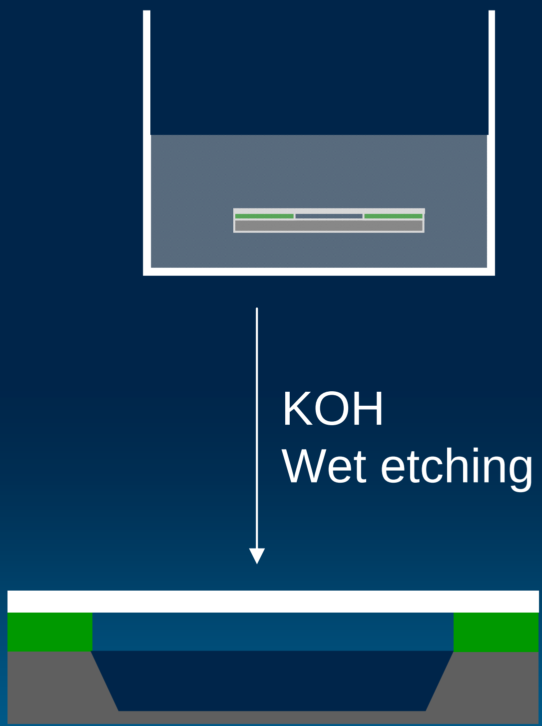
E-beam Lithography (EBL)

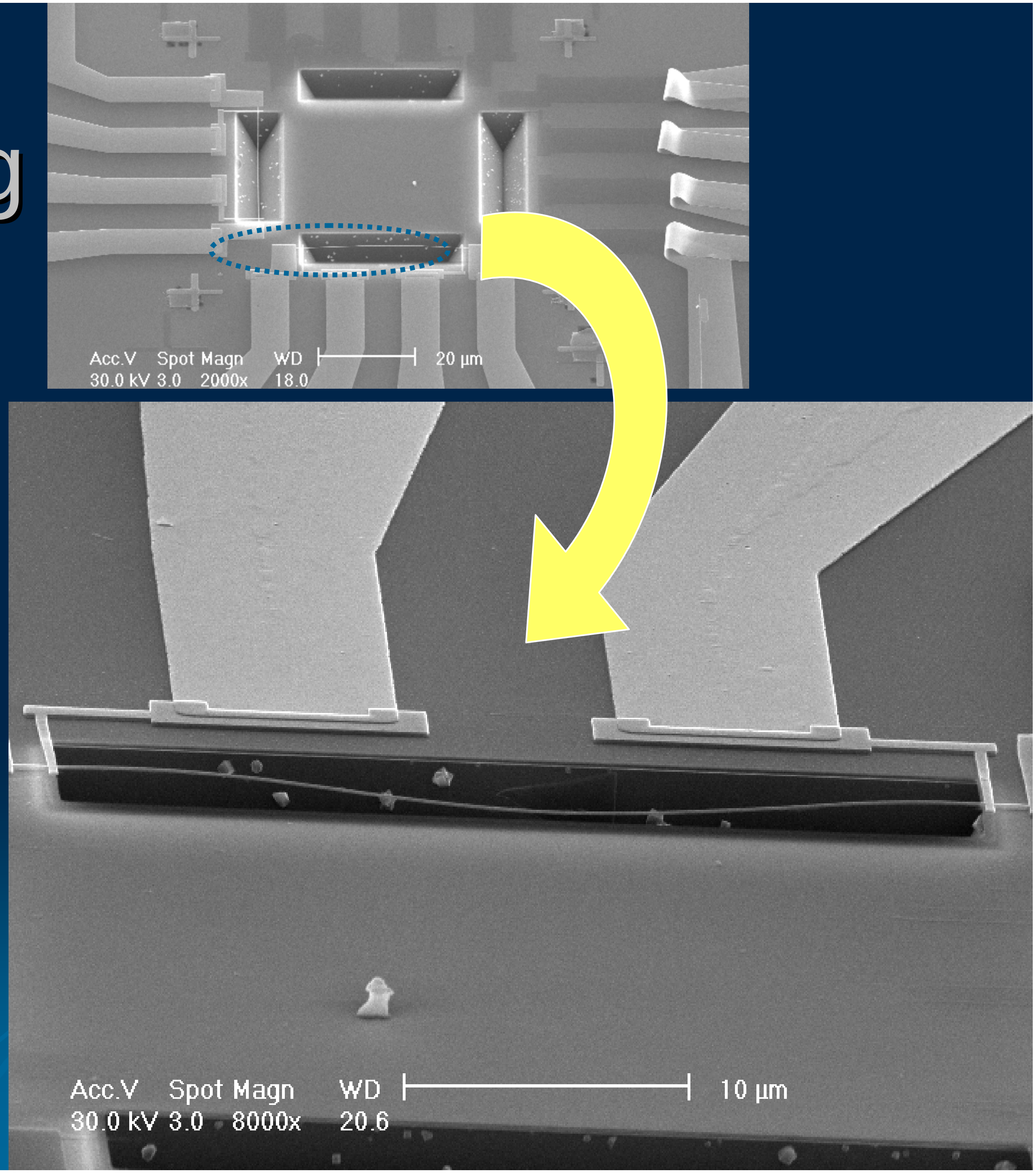


Dry Etching


PMMA
Specimen
Si_3N_4
Si-wafer
1.E-beam exposure
2.Develop
Reactive Ion
Etching (RIE)
CF_4
WD26
15.0kV X40.0K 750nm

Wet Etching


KOH
Wet etching


Acc.V Spot Magn WD 20 µm
30.0 kV 3.0 2000x 18.0
Acc.V Spot Magn WD 10 µm
30.0 kV 3.0 8000x 20.6

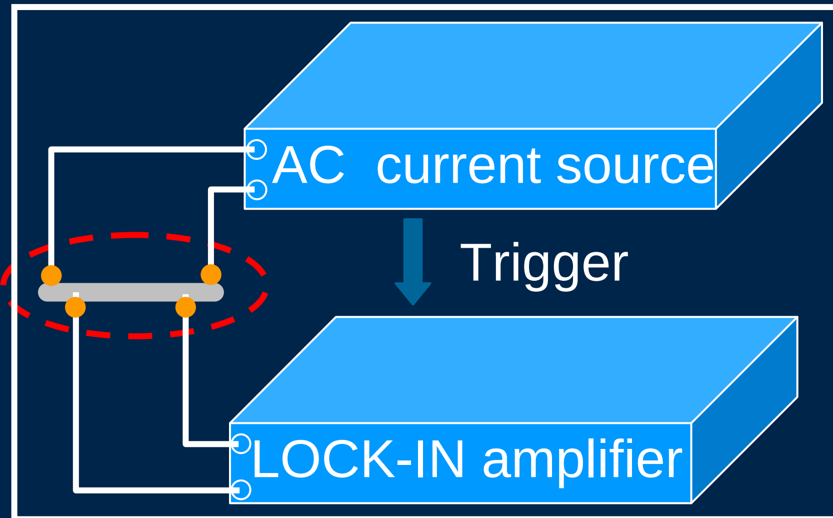
3ω Method for single nanowire

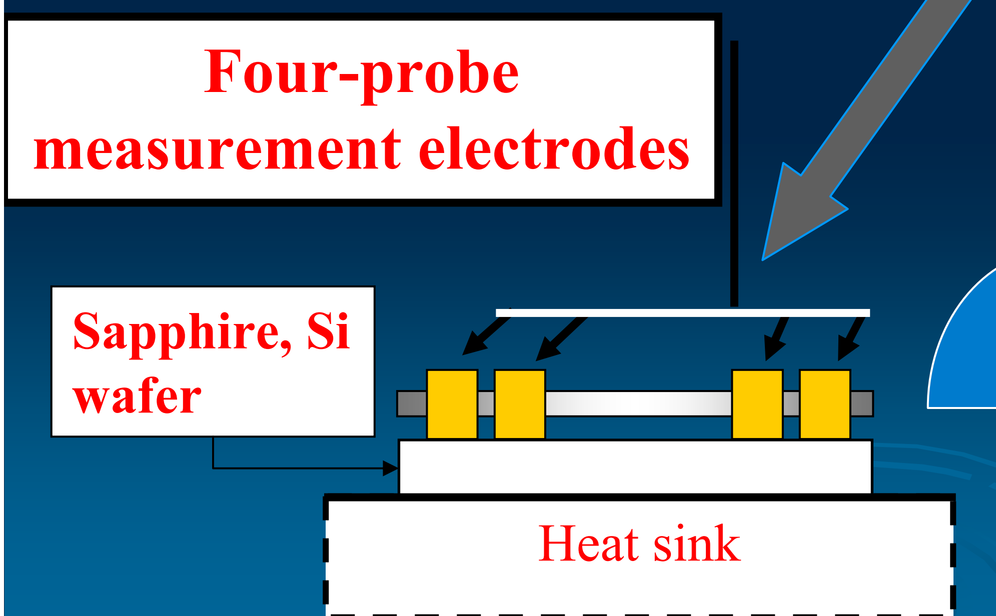
Three requirements

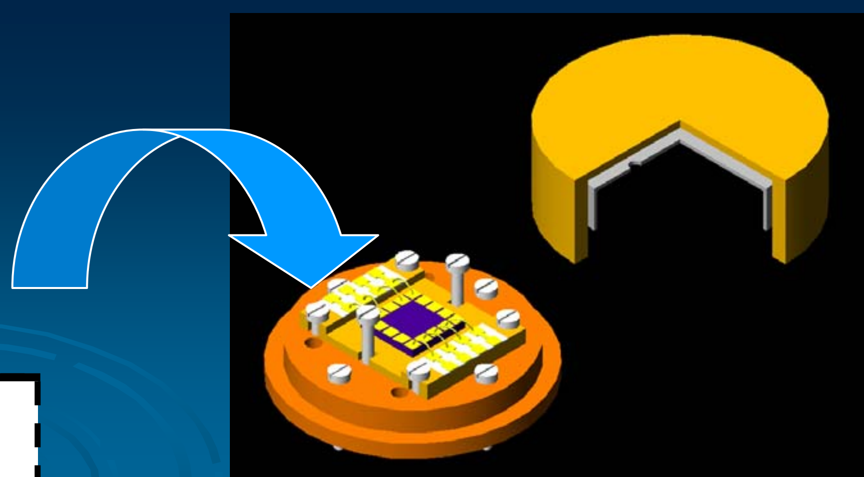
1. Suspended

2. Highly thermal conductive to heat sink

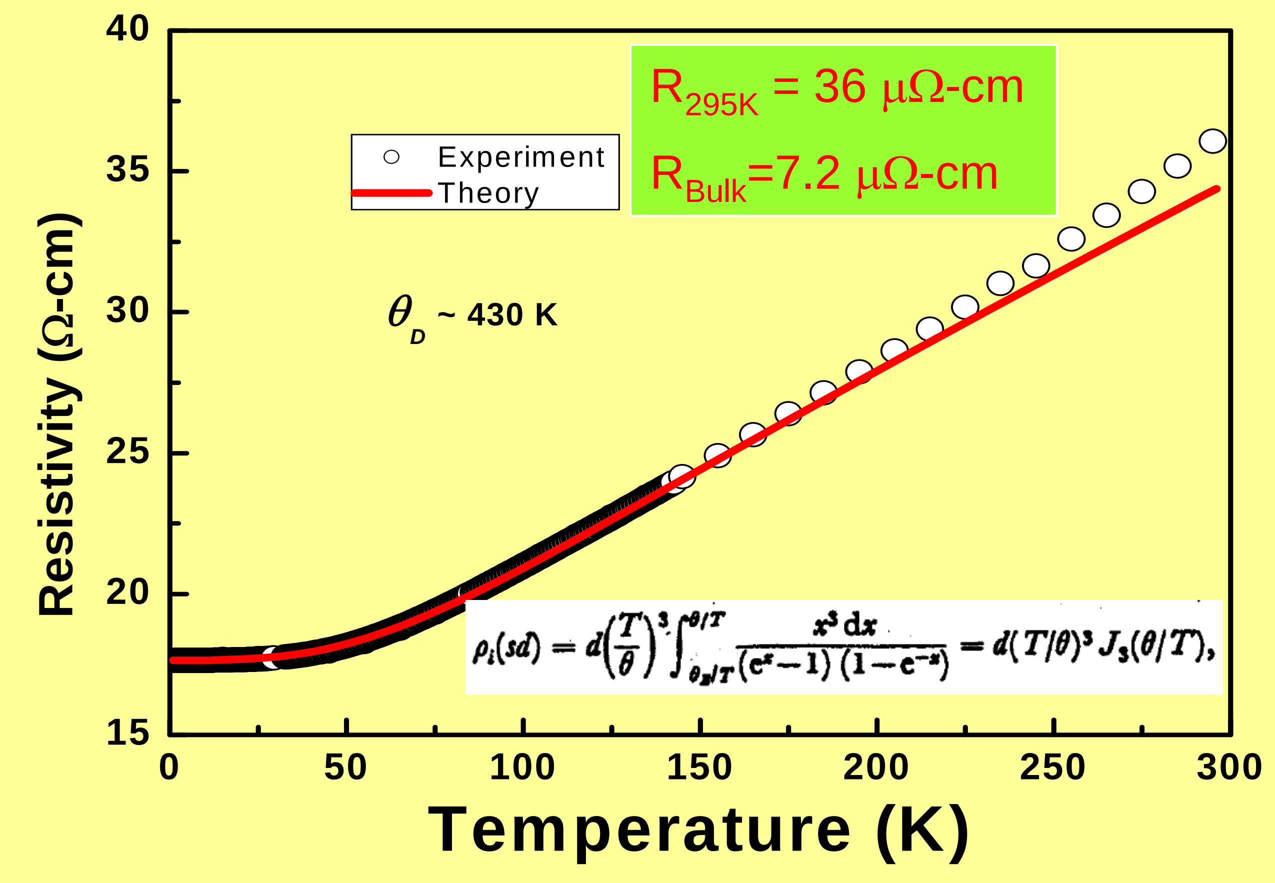
3. Minimize the heat loss







Electrical Resistivity



Relative Resistance Ratio

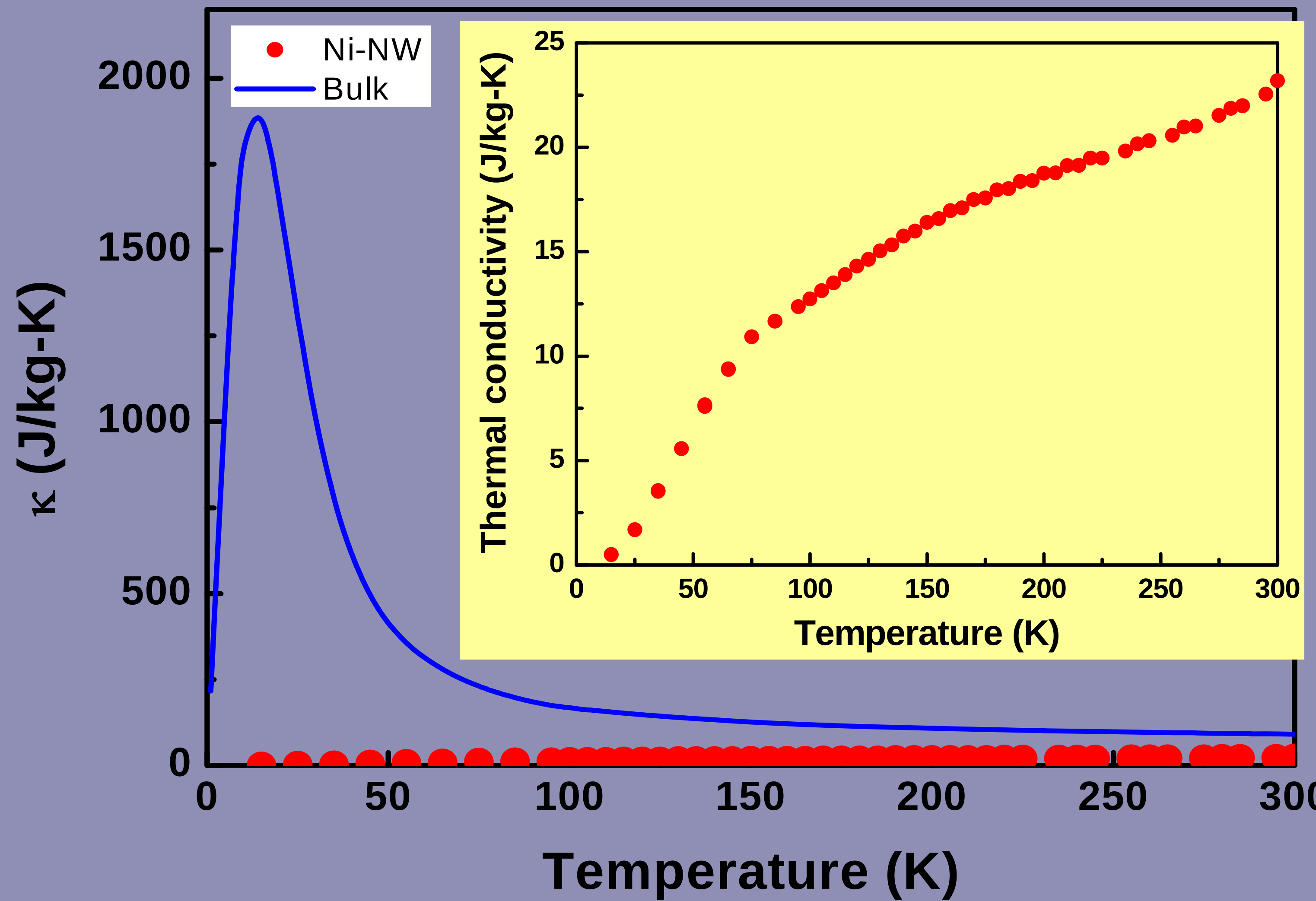
RRR_{295-15} □ 2.04

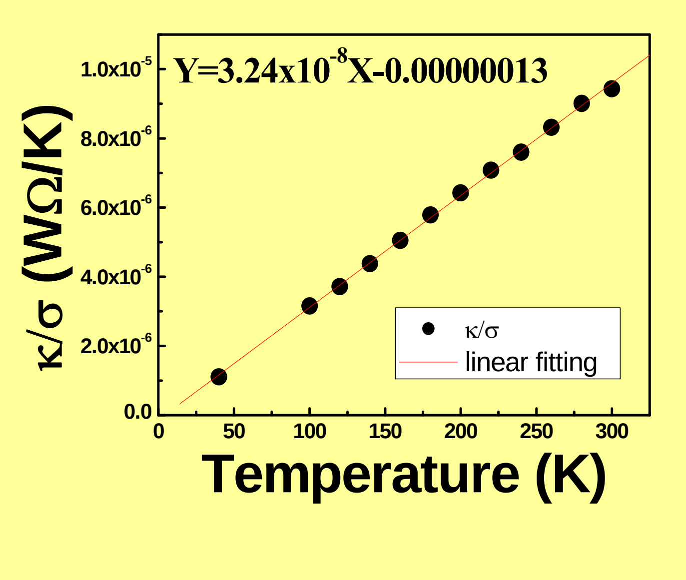
RRR_{pure} □ 47.4

TABLE 5. PHYSICAL DATA

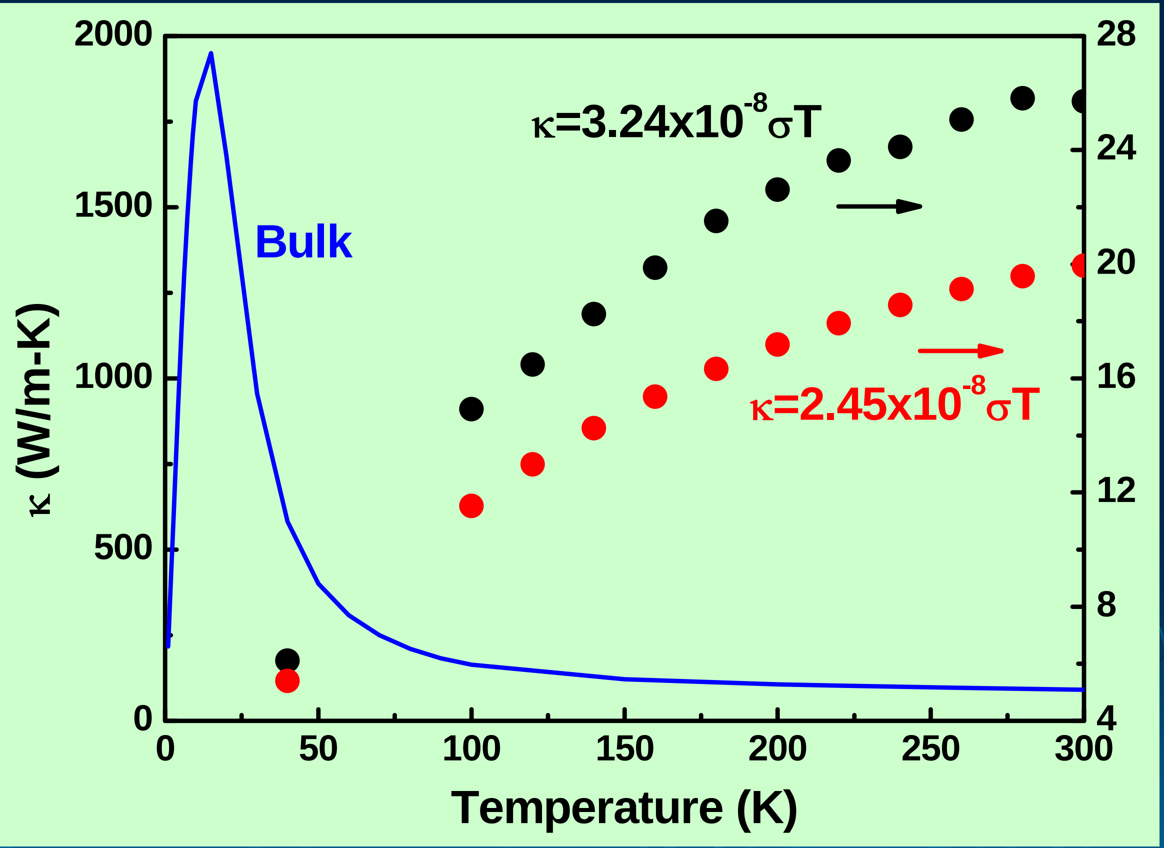
element	structure	M	θ_D (°K)	$\frac{\rho M \theta \Omega^{\frac{2}{3}}}{T}$	λ_{295} (expt.) (W cm^{-1} deg^{-1})	'λ_{295}' $= LT/\rho$	γ (10^{-3} J/mole deg^2)
Fe	b.c.c.	55·85	400	0·7‡	0·82	$0{\cdot}73_8$	5·0
Ru	h.c.p.	101·7	500	1·5	—	$0{\cdot}98_1$	3·3
Os	h.c.p.	190·2	400	2·2	—	$0{\cdot}79_2$	2·3
Co	h.c.p.	58·9	380	$0{\cdot}3_5$‡	—	1·25	5·0
Rh	f.c.c.	102·9	350	0·5	1·51	1·51	4·9
Ir	f.c.c.	193·1	290	0·65	1·46	1·43	3·1
Ni	f.c.c.	58·7	390	0·45‡	0·91	1·03	7·0
Pd	f.c.c.	106·7	295	0·8	0·7	$0{\cdot}68_5$	9·9
Pt	f.c.c.	195·2	225	$0{\cdot}8_s$	0·7	0·69.	6·7

Thermal Conductivity





$$V_{3\omega} \approx \frac{4 I^3 L R R'}{\pi^4 \kappa S \sqrt{1+(2\omega\gamma)^2}}.$$



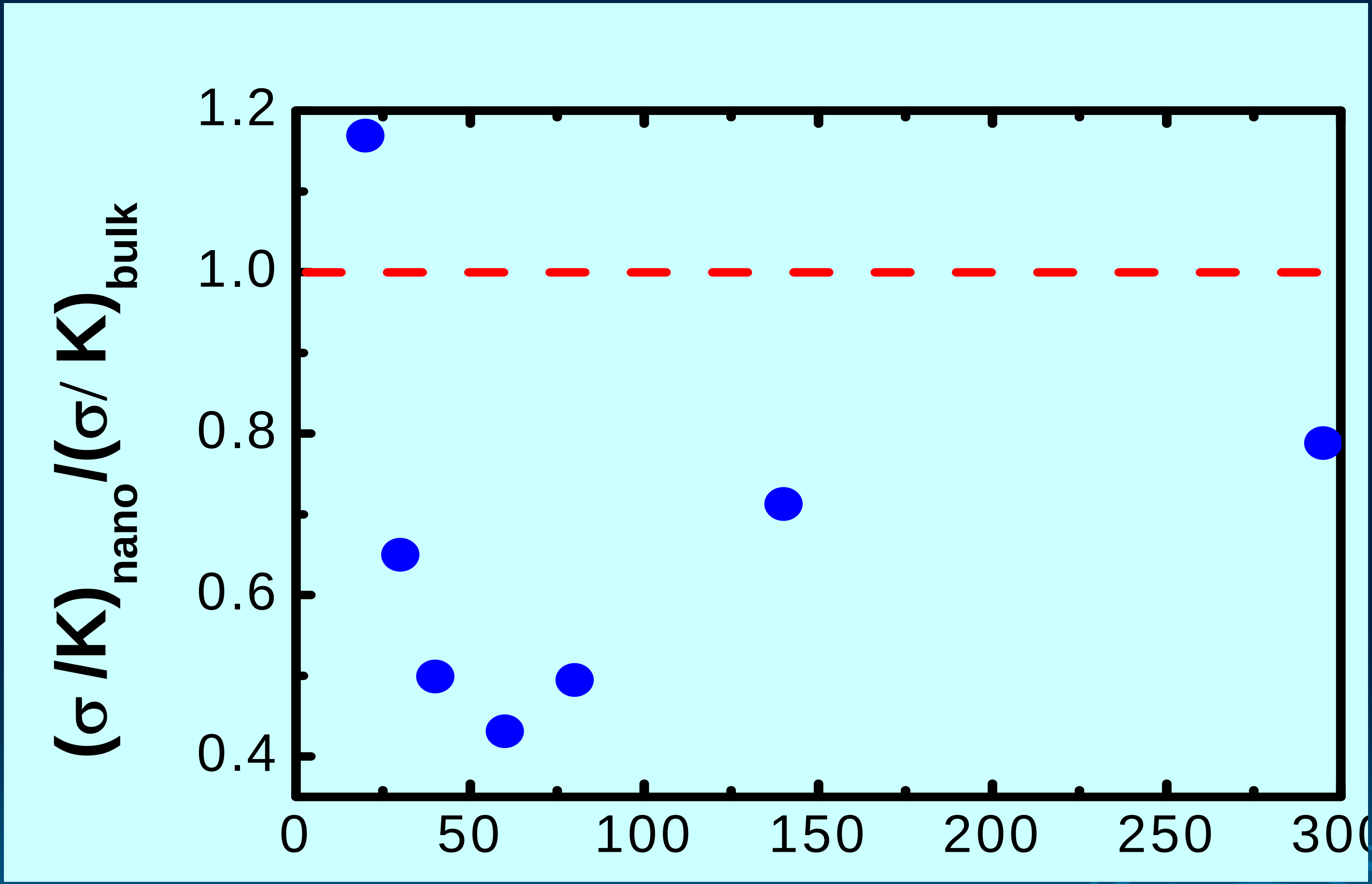
Lorenz number

$$L_0 = \frac{\kappa}{\sigma T} = \frac{1}{3}\left(\frac{\pi k_B}{e}\right)^2$$

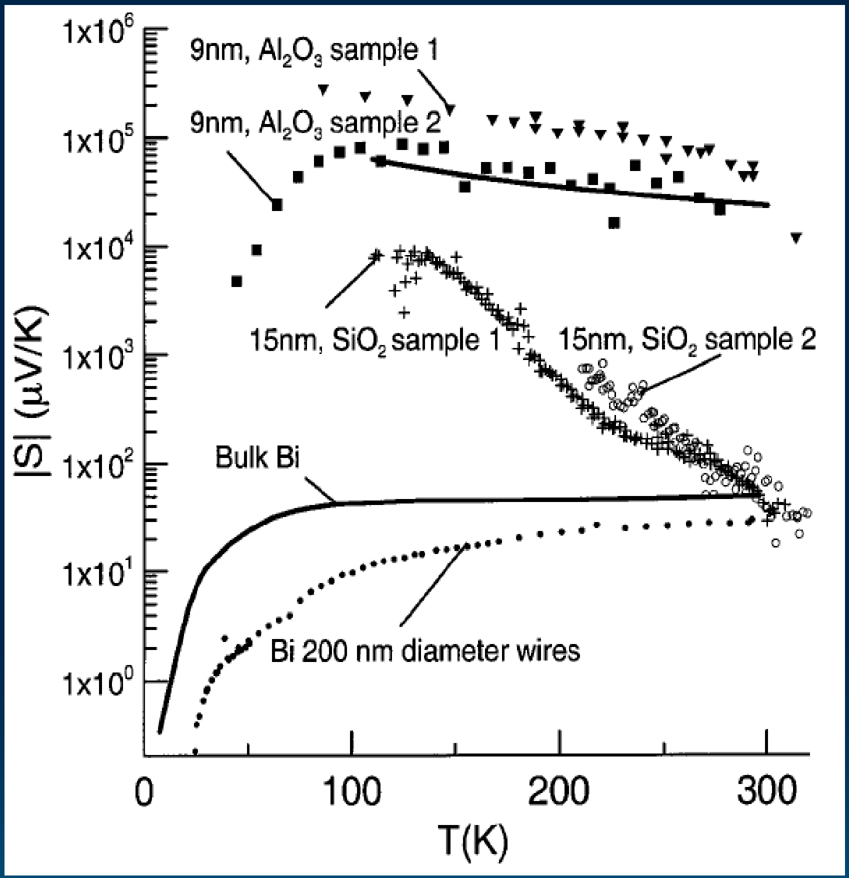
$=2.45\text{x}10^{-8}$ W-Ω/K^2

Wiedemann-Franz law $\kappa_e = \sigma L_0 T$

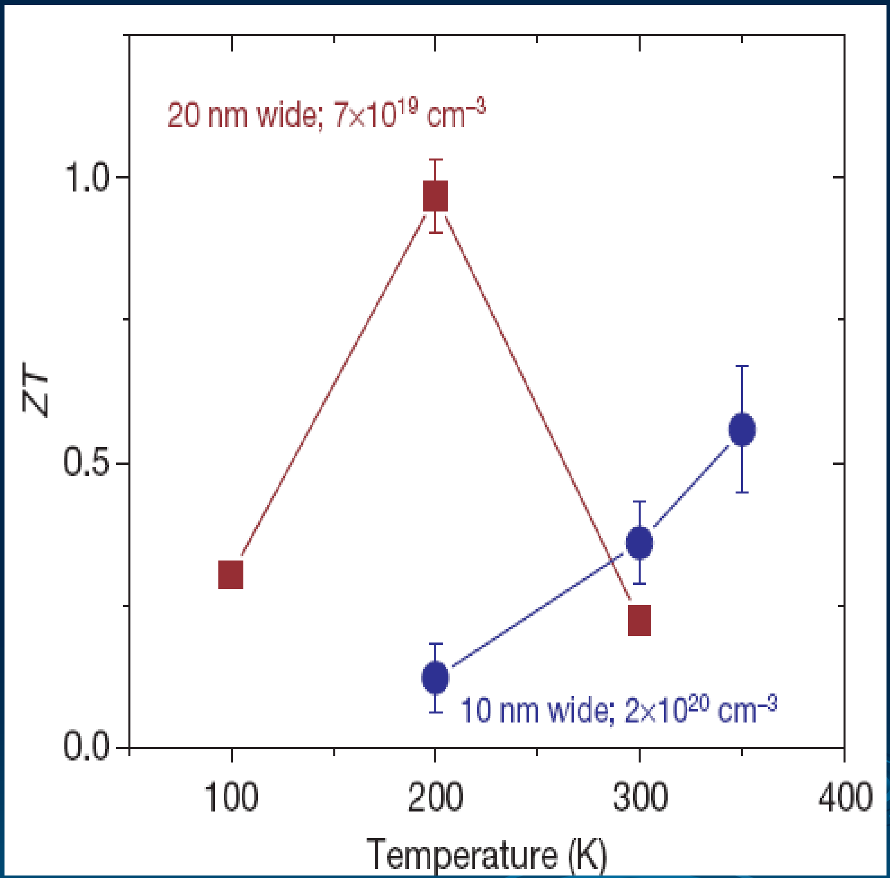
ZT ($\propto \sigma/\kappa$) of Ni-nanowire vs. Bulk



Is the diameter in the quantum size regime? Need to make a smaller diameter wire ~ 10 nm?



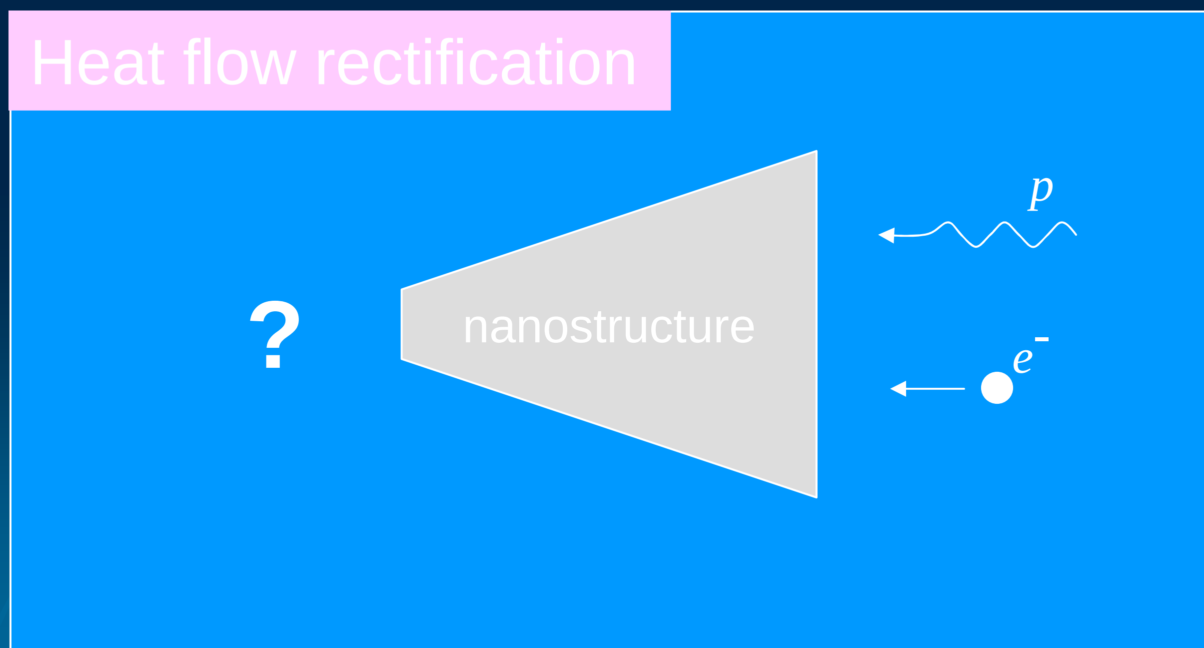
J.P. Heremans, et al., PRL **88**, 216801-1 (2002)

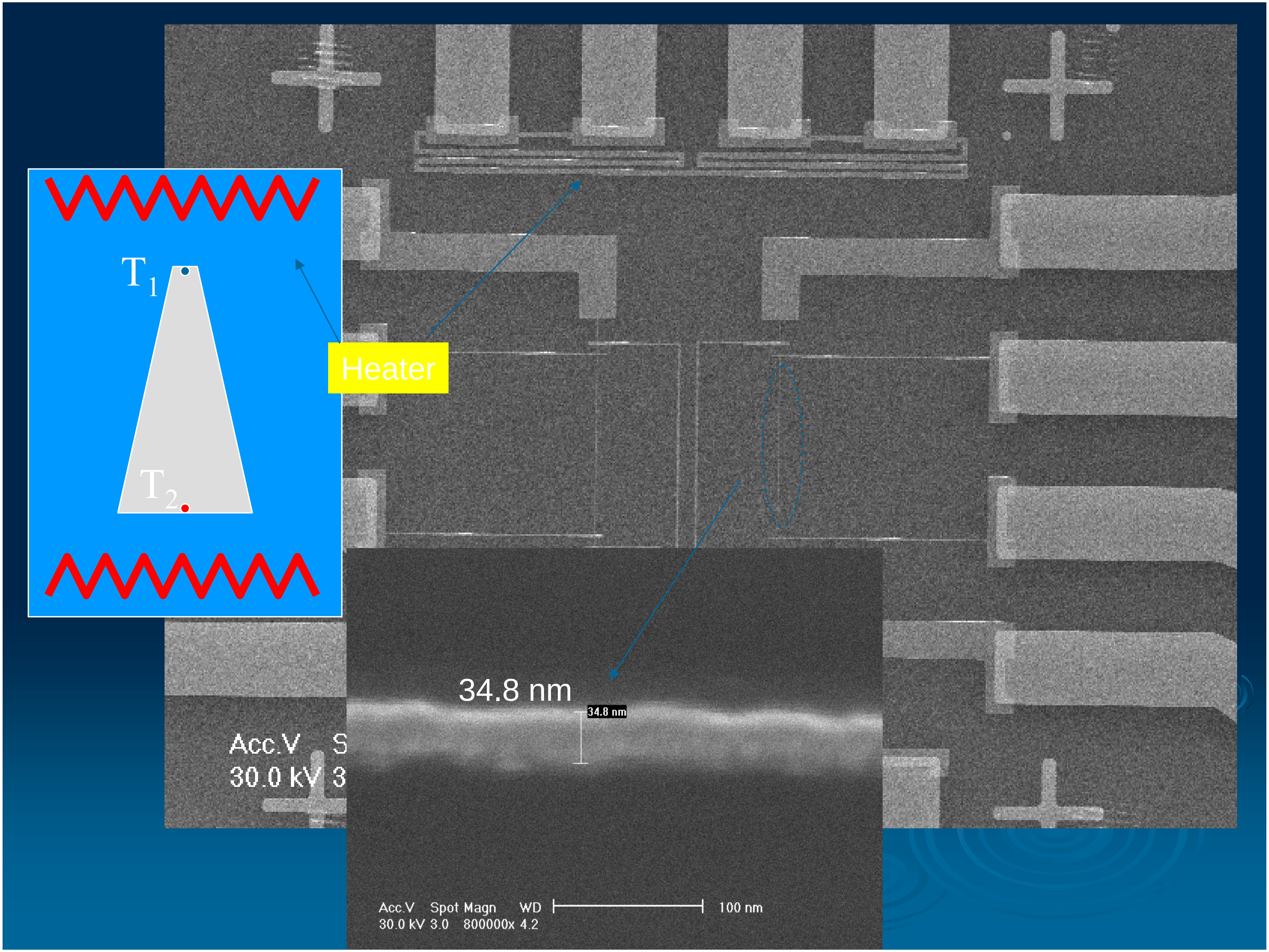


A.I. Boukai, et al., Nature **451**, 168 (2008)

Nanostructures

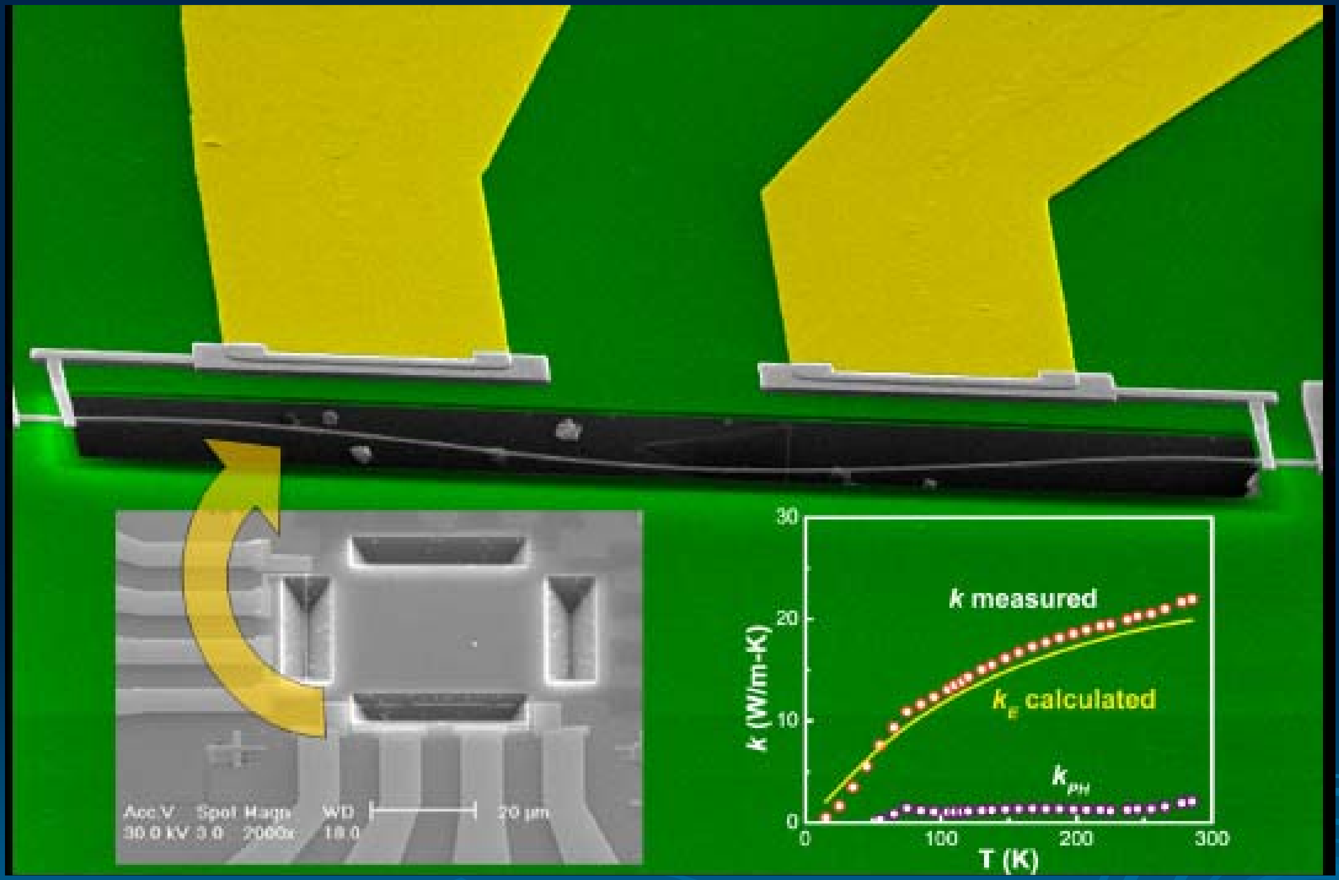
- Transport properties-phonon, electron,…
  - Lattice structure□disorder
  - Dimension□Size effect
  - Spin dependence
  - Shape





Heater
T_1
T_2
34.8 nm
34.8 nm
Acc.V S
30.0 kV 3
Acc.V Spot Magn WD
30.0 kV 3.0 800000x 4.2
100 nm

Thermo-power measurement on a suspended single Ni-nanowire (Φ=200 nm L=10 μm)
Results to appear in APL 2008 Febuary issue



The graph was used on the Cover of APL 11 Feb issue

Summary

- A lithographic process has been developed to construct the suspended structure.
- The self-heating 3ω method and measurement system for nanoscale materials has been constructed.
- The thermal conductivity and specific heat of diameter ~180 nm nickel wire are 23 W/m-K and 64.6 J/mol-K (at 25□), respectively.
- A 30 nm nano-wire has been fabricated to demonstrate our capability